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# Probing the surfaces of heterogeneous catalysts by *in situ* IR spectroscopy†

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This *critical review* describes the reactivity of heterogeneous catalysts from the point of view of four simple, but essential for Chemistry, molecules (namely dihydrogen, carbon monoxide, nitrogen monoxide and ethylene) that are considered as probes or as reactants in combination with “*in situ*” controlled temperature and pressure Infrared spectroscopy. The fundamental properties of H<sub>2</sub>, CO, NO and C<sub>2</sub>H<sub>4</sub> are shortly described in order to justify their different behaviour in respect of isolated sites in different environments, extended surfaces, clusters, crystalline or amorphous materials. The description is given by considering some “key studies” and trying to evidence similarities and differences among surfaces and probes (572 references).

## 1. Introduction: Probing a surface

Heterogeneous catalysts are complex systems whose properties are given by a combination of multiple factors. Activity, selectivity and life-time of the catalyst are determined by the optimum combination of specific features that range from nano to micro and macro properties of the surface properties of the catalyst.<sup>1</sup> A powerful tool to obtain a detailed description of the catalyst surface properties is the use of probe

molecules in combination with an investigative technique able to monitor with the sufficient sensitivity the probe–surface interaction.<sup>2–22</sup> One of the most widely used techniques that follows this approach, is Mid-infrared spectroscopy (4200–400 cm<sup>−1</sup>) using appropriate probe molecules. The method is indirect, in the sense that it monitors the surface through the perturbation inferred to the probe. The observables are the changes in vibrational frequency and intensity of the probe modes. IR-inactive modes can also be observed as a result of the interaction with the surface. In some cases it is also possible to follow induced changes of skeletal and surfaces modes of the catalysts<sup>23–25</sup> and or to follow a reaction-dynamic on the surface.<sup>16,20,26,27</sup> In this respect, time- and temperature-resolved FTIR spectroscopy has the potential to detect intermediate species in a reaction chain.<sup>20</sup> In this contribution we have chosen four probe molecules (H<sub>2</sub>, CO, NO and C<sub>2</sub>H<sub>4</sub>) and for each of them we will report some “case studies” in which they behave as probe molecules and or as reagent.

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† Part of the themed issue covering recent advances in the *in-situ* characterization of heterogeneous catalysts.



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